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Controlled Cathode Electrodeposition

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CONTROLLED CATHODE ELECTRODEPOSITION

by

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IV

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science.

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LIBRARY RESEARCH PROJECT ON CONTROLLED CATHODE ELECTRODEPOSITION

The purpose of this project was to gather data on electrodeposition with controlled potential, and furthermore, to establish a suitable punched-card system for the recording of such data. In the course of the project, it was discovered that the latter took precedence over the former, since it was deemed more vital to have a good punched-card system with fewer data than more data rendered difficult to refer to because of an inefficient system. It must be noted in passing that time and other limitations prevented the completion of a total literature search.

The data to be obtained were to be those which best indicated the electrodeposition potentials of various metallic ions in aqueous solutions of various concentrations. Information regarding the effects of various other factors, such as acidity, temperature, or the presence of other materials, was also gathered. Data concerning the potentials of electrodeposition obtained from fused salts or salts in non-aqueous solutions were excluded.

In regard to the practical importance of such data, the following should be noted. At a given concentration of an ion, a certain minimum voltage is needed to produce electrodeposition. At this voltage, ions of this metal will be reduced and deposited at the cathode until the concentration is reduced to the point where a higher voltage is necessary. Ions of all other metals whose concentrations are sufficient to be deposited at this potential will also plate out, but, unless their deposition potentials are too close to that of the metal under consideration, this may be avoided by removing them by electrolysis at a lower voltage, which is too low to deposit the metal we are primarily concerned with, but high enough for them.

Since, if we set the voltage at exactly that required for the metal at this concentration, it will soon cease to be deposited because of the reduction in concentration, it is best to carry out the electrolysis at a slightly higher potential, care being taken not to raise the potential to the point where other metals will be deposited.

From these considerations it may be seen that it should be possible in most cases to effect the separation of various metallic ions in a solution, provided accurate data concerning potentials needed are available. Of course, the ions must be ones which are capable of electrodeposition in aqueous solution; not, for instance, sodium or calcium.

Previously specific potentials for electrodeposition at various concentrations were obtained chiefly by calculation from the Nernst equation, and based on the assumption that the activity coefficients are either unity or else correspond to those obtained indirectly from other data. Thus it is desirable to have an accurate tabulation of experimental data on the subject.

These data were obtained by searching the literature. Many difficulties were encountered in making this search because of the range of the literature involved. It was found that the most thorough searching technique was that of looking through the entire electrochemistry section of each issue of Chemical Abstracts, and checking all promising articles. This, however, proved to be too time-consuming, so the indexes were employed. It was also found worthwhile to search a couple of specific journals, particularly the Transactions of the Electrochemical Society.

It was found early in the search that most of the articles on practical metallurgy were worthless for our purposes, since they seldom gave more than mere total current, and perhaps current efficiency. It became evident that the really valuable papers were those chiefly concerned with experiments performed with the direct purpose of studying electrodeposition potentials. These data were most useful when expressed directly in terms of deposition potentials, but accurate statements of the relationships between voltage and amperage over a range of current densities were also considered of value.

As mentioned above, the most important element of the project was the establishment of the punched-card system. A punched-card, such as is used for the storage of data, and intended for manual (rather than mechanical) use, consists of a fairly durable, rectangular piece of cardboard with a series of holes punched in one or more rows around the edges. The holes must, of course, correspond exactly to those of the other cards in the series. To prevent the possibility of one card being misoriented by being turned around or upside-down in the file, one corner is usually clipped from each card, so that such a misplacement would be immediately noticed.

As long as the cardboard between a specific hole and the edge of a card remains intact, that card will remain supported when a rod is sent through this hole (and the corresponding holes of the other cards in the series). But should this hole be "notched", that is, should the portion of the card between the hole and the edge be removed, then the card will be free to fall away when a rod through this hole is its only means of support.

The advantages of this system are quite evident. By clipping the proper holes, some, at least, of the information on the card may be tabulated. When only cards referring to one particular type of information are wanted, say, those dealings with one particular element, then by running rods through the proper holes, only those cards will fall away. The advantages over ordinary card filing are that the cards do not have to be kept in any particular arrangement in the file, and that they may be separated according to more than one classification. Thus, beside separating all the cards of one element, we may just as easily separate all at one temperature or within one potential range.

The first difficulty encountered was in obtaining the cards. At first 5" x 8" cards manufactured for this purpose were considered, but these proved too expensive. Since plain 5" x 8" cards could be purchased at one-tenth the cost of the prepared cards, it was suggested that these be employed. But it was feared that it would be impossible to drill these with sufficient accuracy to be useful. Therefore, at first, a system of drop-cards was proposed.

With a drop-card system, a plain card with a series of lines along the edge is employed. A notch is made in the card at the proper line so that, when the series is placed in a properly constructed box, which fits the cards exactly, and which has holes drilled in its sides corresponding to the lines, then this card will fall down over the rod, while the others remain supported and can be removed by passing a rod through a hole which is located in the opposite side of the card and lifting up.

Several objections were raised against this system after some deliberation and experimentation. These were the difficulty in accurately ruling the lines on the cards, and the natural tendency not to notch them properly, as well as the need to construct and use a special box to effect a separation. Therefore, this plan was set aside, and the possibilities of drilling our own cards were again investigated.

Experiments were conducted to determine whether such cards could be drilled properly on a small scale. Two double rows of holes (sixty-two holes in all) were drilled into about one hundred and fifty 3" x 5" cards with an electric hand drill, using a heavy pasteboard template. The following defects were noted: a tendency for the template to wear out; difficulty in drilling straight through the deck; and a strong tendency for the rims of the holes to bulge out in such a manner that the cards supported each other, thus preventing them from falling away freely.

Since it was felt that the first two difficulties could be avoided by using a metal template and a supported drill, it was decided to try a large-scale production of

8" x 5" cards, using the equipment in the College machine shop. One of the commercially available cards with one side of double holes and three sides of single holes was used as a model, and a template was constructed of hardened aluminum. It was found that there was no difficulty involved in drilling straight, and, although some wear on the template was reported, several thousand cards have been drilled so far without need of a replacement. As to the tendency to bulge, this was negligible, except in cases when the drilling was done too rapidly. Thus, cards produced in this manner were the ones finally adopted.

Next it was necessary to determine the manner of coding to be employed. Here it was a question of choosing between convenience and maximum utilization of hole space. It is possible to store a great deal more information with one set of holes by adopting certain methods of coding which involve maximum utilization but which necessitate repeated needling to obtain only the right cards, than by using a system designed for convenient needling.

The small, home-made cards mentioned above were used to experiment, using a maximum utilization system. A double row of three holes apiece were numbered as follows:

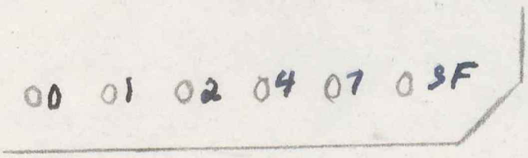
01 03 09

01 03 09

By punching these either deep or shallow, any number from 1 through 26 may be obtained, but, upon needling for any specific number, other numbers will fall out, and so the cards obtained must be re-needled to eliminate these. For example, if the card desired is #7, one would first have to needle through shallow 1 and deep 3, obtaining not only #7 but also #s 8, 16, 17, 24, and 25. It would take two extra needlings, once removing all that fall off when needled through shallow 9 (i.e. #s 16, 17, 24, and 25), and again through deep 1, removing all that fall off (#8), to obtain pure #7.

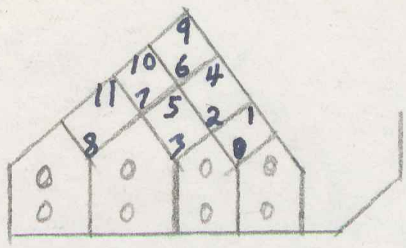
On paper, even more complicated systems were worked out. The one mentioned above, using the numbers to represent the first letters of authors' names, was tried experimentally with about fifty cards, and its obvious defects were soon recognized. Therefore, a slight modification of another system was the one finally employed.

In this system, sither six holes in a single row or four pairs in a double row are used to obtain a single digit, and all numbers of more than one digit are coded under the separate digits, rather than trying to express the whole number with one set of cuttings. The advantage here is that but one needling (using a pair of needles simultaneously) is all that is needed to obtain one digit exclusively. The arrangement is:



The letters SF stand for "single function", indicating that the other number cut is the same as the digit required. This way two needles are always used and no other numbers except the one desired appear. Otherwise, if a single number such as 4 were desired, 4 + any other number in the series would also be obtained; in this case, 4 + 1 - 5 and 4 + 2 - 6. It would be possible to avoid this by punching 4 + 0 ; this would work in every case save 0 itself.

With a group of four double holes, a triangular field is used:



The card is to be punched twice in each field. The punch on the left shows which symbol is intended.

In order to see how the information is tabulated on the cards, please observe the arrangement on the attached sample card.

Explanations:

1. Atomic number of element - two digits.
2. Author. The attached alphabetical list of beginnings of names, going from 1 to 99, has been prepared with the aid of a larger list (1 to 1,000) obtained from the McBee Company.
3. Voltage range must be expressed, although it does consume space, since most articles involve more than one potential. Voltage is measured in centivolts against a saturated calomel electrode. Extra hole is punched if the value is negative.
4. Main substance added. The number equals the atomic number of the interferring ion. An acid acting only as an acid is placed under H (1). If two metals are present, the one with the larger concentration is classified as the main element and the other as the interferring substance, regardless of which is actually being plated out. The only exception to this rule occurs when a salt of an alkali or alkaline earth metal is added merely as a source of negative ions. In this case, the substance is classified under the most important element of the negative ion. E.g: $NaNO_3$ goes under nitrogen.

The numbers above 92 are used to indicate the following:

93- all elements above 92.

94- alcohols.

95- aliphatic compounds.

96- aromatic compounds.

97- gelatinous substances.

98- miscellaneous substances (organic).

99- miscellaneous substances (inorganic), or mixtures of salts.

5. P- ion must also be expressed as a range, as well as:
6. pH. Should either be only one figure, only the set to the left is to be cut. pH above 11 is considered as 11.
7. The number under Temperature equals the temperature in degrees centigrade divided by 10. Decimals thus obtained are always coded under the number before the decimal point. Thus, 29^{o}C is coded under 2. If a range of temperatures is given, the card is coded according to the highest.

Addenda:

99 ALPHABETICAL SUB-DIVISIONS

1-A	51-Li
2-Al	52-Lo
3-Ar	53-Lu
4-B	54-M
5-Ban	55-Mar
6-Bas	56-Mas
7-Bel	57-Mc
8-Bi	58-McG
9-Bl	59-Me
10-Bo	60-Mi
11-Br	61-Mo
12-Bri	62-Mor
13-Brown	63-Mu
14-Bu	64-N
15-C	65-Ni
16-Ch	66-O
17-Co	67-Om
18-Cook	68-P
19-Cr	69-Pe
20-D	70-Ph
21-De	71-Pr
22-Di	72-R
23-Dor	73-Re
24-Du	74-Ri
25-E	75-Ro
26-Em	76-Ru
27-F	77-S
28-Fe	78-Sc
29-Fl	79-Schu
30-Fr	80-Se
31-G	81-Shi
32-Ge	82-Sk
33-Gl	83-Smo
34-Gr	84-Sp
35-Gro	85-Sti
36-H	86-Su
37-Har	87-T
38-He	88-Th
39-Hi	89-Tr
40-Ho	90-U
41-Hu	91-W
42-I	92-Wam
43-J	93-We
44-Jones	94-Wh
45-K	95-Wi
46-Ki	96-Wo
47-Kn	97-Wr
48-Kr	98-Y
49-L	99-Z
50-Le	

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